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A STUDY OF HUMUS IN HAWAIIAN SOILS.

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THE DETERMINATION OF HUMUS.

INTRODUCTION.

During recent years considerable attention has been given to a study of methods for the determination of the ammonia-soluble organic matter in soils. In these investigations some modification of the method originally proposed by Grandeau has usually been employed. In practically all the methods now used the soil is treated with a 4 per cent solution of ammonia after removing the calcium and magnesium by the preliminary extraction with dilute hydrochloric acid, the solution thus obtained being considered the humus solution. In this paper the term "humus" is used to signify the organic matter of soils soluble in a 4 per cent solution of ammonia after removing the calcium and magnesium with dilute hydrochloric acid.

The Hilgard method¹ is a slight modification of the original method as proposed by Grandeau and consists in the pre-

1. U. S. Dept. Agr., Bur. Chem. Bul. 38, p. 80.

liminary treatment of the soil with a 1 per cent solution of hydrochloric acid on a funnel, after which the soil is extracted with a 4 per cent solution of ammonia until the extract is colorless. During this process the surface of the soil is protected from puddling by a disc of filter paper. The filtrate is then evaporated to dryness and incinerated, the loss upon ignition being expressed as humus.

The method of Huston and McBride¹ consists in shaking 10 grams of soil for a definite length of time with a definite volume of 4 per cent solution of ammonia, after the preliminary extraction with dilute hydrochloric acid. The solution, upon standing 12 hours, is filtered, and an aliquot evaporated to dryness and incinerated as in the Hilgard method. This method, with slight modifications, has been adopted by the Association of Official Agricultural Chemists and will be hereafter referred to as the official method.

For some time it has been recognized that the official method frequently gives abnormally high results, and as has been shown by a number of investigations, this is due to the fact that the clay becoming deflocculated by ammonia can not then be removed by ordinary filtration, and upon evaporating to dryness the solution thus obtained, the clay still contains water of hydration which can not be completely driven off at temperatures below the point of decomposition of the organic matter. Upon incineration, however, this combined water is driven off along with the organic matter, thus giving too high results. Various methods for separating the clay from the humus have been proposed. Cameron and Breazeale² used a Pasteur-Chamberland filter; Peter and Averitt³ deducted from the humus 10 per cent of the humus ash; Mooers and Hampton⁴ coagulated the clay by repeated evaporation on a water bath; Stoddart⁵ coagulated the clay by use of ammonium sulphate after which he precipitated the humus with hydrochloric acid; Fraps and Hamner⁶ used a solution of potassium chlorid to coagulate the clay; Rather⁷ attempted to make the separation by means of electro-

1. U. S. Dept. Agr., Bur. Chem. Bul. 38, p. 80.

2. Jour. Amer. Chem. Soc., 26 (1904), p. 29.

3. Kentucky Sta. Bul. 126, p. 122.

4. Jour. Amer. Chem. Soc., 30 (1908), p. 805.

5. Jour. Indus. and Engin. Chem., 1 (1909), p. 72.

6. Texas Sta. Bul. 129.

7. Texas Sta. Bul. 139.

lysis and found that a change in the composition of both the organic and inorganic constituents took place. In addition, he proposed a new method, which consists in coagulating the clay by the use of ammonium carbonate, a salt which is volatile below 100° C. This method has been studied recently by the associate referee on soils for the Association of Official Agricultural Chemists. Recently Wells, Stevenson, and Coover¹ made use of a centrifuge in separating the humus from the clay.

A number of investigations of these methods have been made during recent years, and while practically all are agreed that the official method is unreliable, conflicting reports as to the reliability of other methods have been issued. In a critical study of this question, Alway, Files, and Pinckney² compared the Hilgard, official, Cameron-Breazeale, and Mooers-Hampton methods with twelve different soils from Nebraska and concluded from their experiments that the official method is wholly unreliable, while the methods of Hilgard, Mooers-Hampton, and Cameron-Breazeale (when slightly modified) are accurate.

EXPERIMENTAL.

In connection with soil studies in this laboratory, considerable time has been devoted to the determination of the so-called humus in Hawaiian soils and it has been recognized for some time that the results obtained by the use of the official method are unreliable. The soils under investigation were taken from the upper lands of the islands, and while extremely variable, frequently contain a very high percentage of clay. In addition, the clay exists in a state of very fine division. It is a common occurrence to find soils, the clay content of which will remain in suspension indefinitely when shaken with distilled water. This study led to an investigation of the methods previously employed in humus determinations.

The soils used in this investigation represent a wide range in composition and properties. The humus, as will be shown varies from 2.64 per cent to 18.27 per cent and the mechanical analyses show a varied physical structure. Since the chief difficulty in humus determinations is associated with the clay, the mechanical composition of the soil used is of some interest.

1. Iowa Sta. Bul. 124.

2. Nebraska Sta. Bul. 115.

The following table gives the results of mechanical analysis of the soils.¹

Mechanical analysis of soils used in experiments.

	SOIL NUMBERS.										
	69.	74.	97.	98.	99.	100.	101.	102.	103.	104.	108.
	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>
Organic & Combined water ...	44.60	25.83	14.32	13.65	15.80	15.55	13.06	14.67	17.58	16.17	15.55
Fine Gravel.....	5.94	1.64	.09	.12	.86	.41	.14	0.29	.06	.09	.96
Coarse Sand.....	26.72		.43	.43	.73	1.65	.50	0.91	.26	.42	
Fine Sand	8.65	38.03	1.62	2.11	2.35	1.65	1.33	1.12	.81	2.36	13.58
Silt.....	4.07	16.22	3.37	3.06	9.28	6.72	6.23	7.38	5.60	6.44	6.25
Fine Silt.....	5.09	19.99	27.19	26.32	32.69	18.45	28.88	18.87	22.70	29.07	13.35
Clay.....	5.78	2.05	52.30	55.05	38.60	57.80	47.45	57.80	56.72	44.54	51.26

From the above analysis it will be seen that some of these soils contain very high percentages of clay and fine silt, both of which will remain in suspension for some time. A pronounced characteristic of Hawaiian soils is a very high content of iron, which usually imparts to the soil a red color. In connection with humus determinations, it is important to know not only the amounts of clay in the soil, but something regarding its properties, for, as will be shown presently, clay is a sort of generic term when applied to soils, and usually has reference to the size of the particles and does not imply definiteness regarding their composition and properties. From analyses made in this laboratory, we consider the clay in Hawaiian soils as a mixture of several substances, some of which, perhaps, rarely occur in soils, but which have a decided bearing on the applicability of methods for the determination of humus.

In all humus determinations reported in this bulletin, except as otherwise stated, the solutions were made according to the official method, and when the entire determination was completed by the use of this method the results obtained were as follows:

1. Analyses made by the method as outlined by Hall. *The Soil*. London, 1908, 2. ed., p. 51.

Determinations made by official method showing abnormally high humus ash.

	SOIL NUMRERS.							
	97.	98.	99.	100.	101.	102.	103.	104.
	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>
Humus.....	4.30	5.94	5.12	6.38	4.64	4.34	6.31	3.54
Humus Ash.....	13.25	20.92	10.54	33.20	15.18	13.15	25.42	7.67

The above data were considered unreliable for two reasons: (1) the percentages of humus are considerably higher than the general properties of these soils would indicate; and (2) the humus ash is many times higher than the humus could possibly contain as mineral matter chemically combined with it. In addition, the humus ash in each instance was found to be red in color and similar in appearance to the clay in these soils. From these results it is at once apparent that the official method is likely to be inaccurate when applied to such soils.

This investigation has led to the study of a number of the most important methods previously used in the determination of humus, and from this study it seems that under certain circumstances a number of these methods will give reliable results. A partial explanation of the disagreement among the several publications dealing with this subject is probably found in the fact that the soils studied were very different in composition and properties. If this assumption be true, it then becomes a matter of both practical and theoretical importance to know the properties of the soil at hand, and if possible, find a method that is universally applicable.

Among the methods used in these investigations are those of Hilgard, Mooers and Hampton, Cameron and Breazeale, and Rather. Since the chief difficulty to be overcome in humus determinations is that of removing the clay, the humus ash has been determined in each instance. The following table shows the results as obtained by the use of the several methods:

Comparison of several methods in present use.

HUMUS.

Method.	Soil numbers.										
	69.	74.	97.	98.	99.	100.	101.	102.	103.	104.	108.
	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>
Official.....	4.30	5.94	5.12	6.38	4.64	4.34	6.31	3.54
Hilgard.....	15.63	5.26	2.43	2.61	3.68	2.95	2.71
Mooers-Hampton....	18.74	5.32	2.68	2.70	3.17	2.32	3.72	3.20	3.72	2.68	3.84
Cameron-Breazeale.	12.30	3.98	2.34	2.38	2.91	2.24	2.85	2.24	2.94	2.36	2.20
Rather.....	20.75	6.49	4.32	4.15	5.01	6.03	5.64	4.38	5.95	4.81	8.24

HUMUS ASH.

Official.....	13.25	20.92	10.54	33.20	15.18	13.15	25.42	7.67
Hilgard.....	5.44	1.85	2.46	2.56	2.00	4.28	1.82
Mooers-Hampton ...	6.33	1.33	.60	.84	.65	.41	1.52	1.70	.98	1.17	.44
Cameron-Breazeale.	1.09	1.81	.28	.74	.33	.33	.31	.30	.57	.23	.46
Rather.....	7.71	2.51	12.94	11.43	10.40	25.69	17.61	10.28	20.49	12.74	32.69

From these results, it is evident that there is a wide range of variation in the percentage of both the humus and humus ash when determined with the various methods, and that a strict concordance does not exist between the results obtained by any two methods. It is true the results obtained by the use of the Hilgard, Mooers-Hampton, and Cameron-Breazeale methods are in fair agreement in certain instances, but on the whole they are too discordant to permit their indiscriminate use. By reference to the humus ash it will be seen that none of these methods save that of Cameron-Breazeale effected a complete removal of the clay in every instance. The Rather method, in most instances, brought about no coagulation of the clay whatever, and therefore, in its original form, can not be relied upon with these soils. By the use of the method of Mooers-Hampton it was found to be necessary to evaporate the humus solutions to dryness, in some instances as many as six times, allowing the residue to bake at the temperature of boiling water for some

hours after becoming dry, and even then a partial deflocculation of the clay upon complete resolution in ammonia was unavoidable. In the main, however, this method can be manipulated so as to remove the clay, at least to the point where it is of small importance. The time required, however, together with the fact that the evaporations have to be made in an atmosphere free from acid fumes, makes the method tedious and impracticable. There is evidence, as will be shown later, that a partial oxidation of the humus also takes place.

The method of Cameron and Breazeale, while originally not proposed as a quantitative method, has been studied by a number of chemists, the results of which show it to be an effective means of removing the clay, but one that is likely to bring about a change in the concentration of organic constituents. The apparatus previously employed makes use of increased pressure supplied by means of compressed air and the solution is forced through a Pasteur-Chamberland tube from an annular space connected with a compression chamber, and is collected from the tubular part of the filter which projects from a close fitting joint below. When solutions are made to volume previous to passing through the filter, and an aliquot taken after passage, considerable difference in the concentration is likely to be observed. Variation in the pressure, as well as different tubes, affect solutions unequally. The effect of the tubes is due to two causes: first, the clay filter has the property of absorbing substances from solutions, especially organic compounds; second, the clay may act as a semipermeable membrane, thus permitting some substances in solution to pass through unchanged, while the concentration of still others is modified.

The humus solution is a complex mixture and, as will be pointed out later, varies greatly from soil to soil so that it seems unlikely that a factor could be found that would compensate for the changes produced in the ordinary passage through a clay filter. The effects produced by the clay filter on the humus solution appear to be largely in the nature of absorption and upon passing the solution through for some time an equilibrium is established between the solution and the filter, and no further change occurs. Some humus solutions, of about 500 c. c. vol., were passed through such a filter, an aliquot of 75 cubic centimeters removed, and the remaining volume again passed

through the filter. This process being repeated several times and aliquots removed after such passage as above. These aliquots were evaporated to dryness and incinerated and the results are recorded in the following table:

Effect of repeated filtration through clay filter:

HUMUS.

Soil samples.....	Number of successive filtrations						Amounts present in original solutions.....
	1.	2.	3.	4.	5.	6.	
	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>
101	1.97	2.06	1.99	2.20	3.61
102	2.28	1.80	2.20	2.10	2.02	2.02	3.37
103	2.40	2.58	2.32	2.34	2.40	2.52	4.74
104	2.24	2.28	2.60	3.22

HUMUS ASH.

101	0.07	0.06	0.10	0.0678
102	.34	.30	.54	.28	0.20	0.32	.70
103	.18	.36	.46	.30	.32	.36	1.12
104	.78	.72	.3676

From these data it is apparent that a pronounced change in the concentration took place during the first passage, whereas successive filtrations produced little further effects.

For example, sample No. 102, whose actual humus content was 3.37% (determined by Mod. Clay Filter method) on passing through the clay filter according to the ¹Cameron and Breazeale method was found to be only 2.28%, or a loss of 1.09%. On repassing this filtrate through the same filter and taking aliquots after each passage there was practically no more absorption of organic matter after the first filtration. This fact indicates the possibility of a state of equilibrium between the filter and humus extract.

1. Loc. cit.

Alway¹ and his associates overcame the difficulties attending the use of the clay filter by passing a definite portion of the solution through the filter then forcing through a 4 per cent solution of ammonia until the filtrate contained no organic matter. The solution and washings thus obtained were combined and made to volume and aliquots evaporated to dryness for the determination of humus. In this study these investigators found this modification of the clay filter method reliable and accurate, but they state that it is too tedious to be of practical value.

A MODIFIED CLAY METHOD.

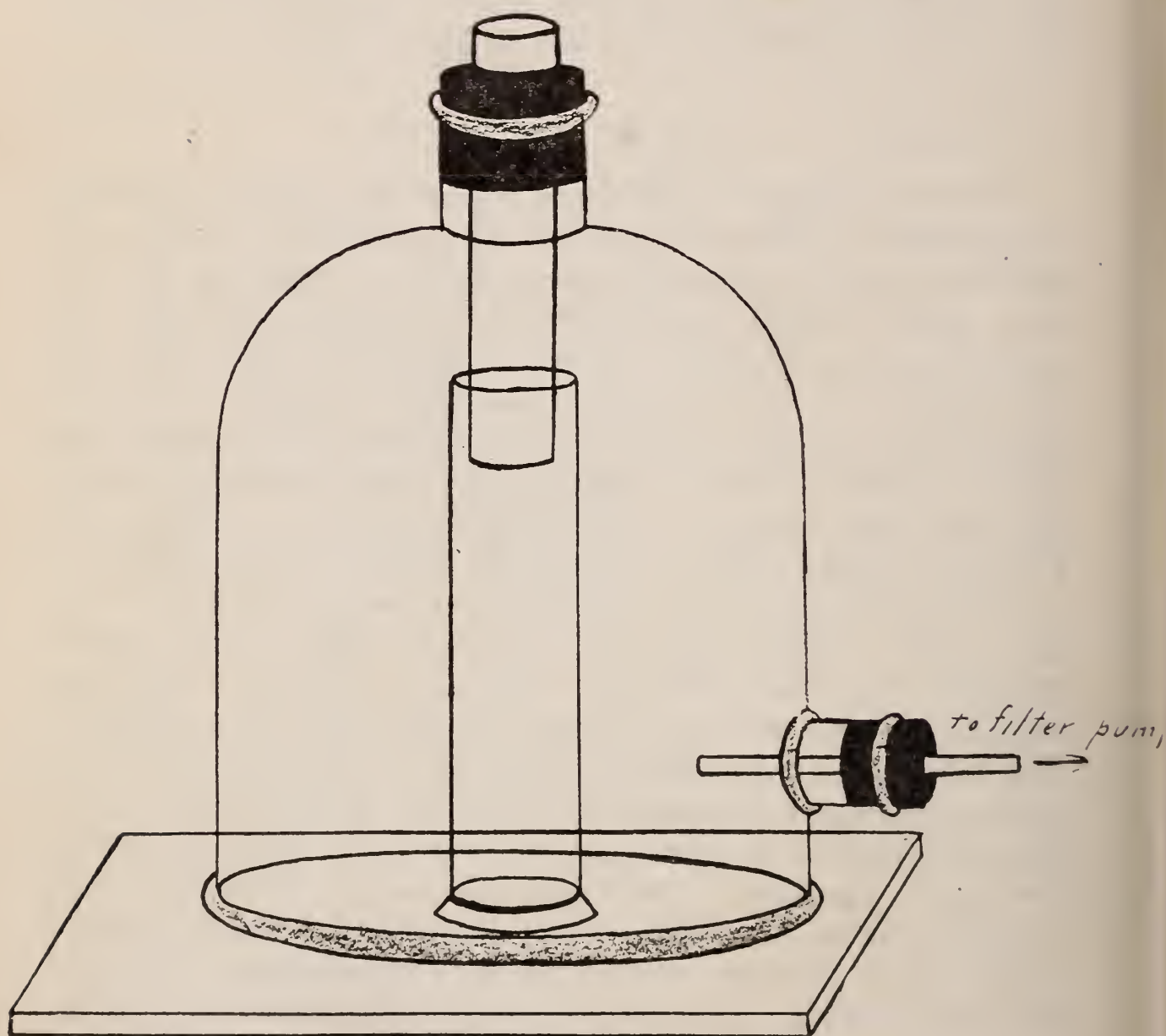
From the failure to effectively remove the clay by any other means than by the use of the porous clay filter, attention was directed toward overcoming the difficulties attending its use. As a result a slight modification of the method of Alway and others has been found to be both effective and practical, and with which it is, we believe, possible to secure accurate results with any soil. The essential feature of the method consists in passing a definite aliquot of the humus solution through the filter, then forcing through ammonia until the solution contains no organic matter, as was done by Alway and others.

The difficulties of this method have been overcome as follows: The solution is drawn through the filter in the reverse direction from that ordinarily employed. Instead of using the compression chamber, an ordinary suction pump was employed. The tube of glazed porcelain, attached to the lower end of an eight-inch Pasteur-Chamberland tube, was broken off so as to leave this end of the tube open; then the tube was inserted into the upper opening of a bell jar, such as is used for filtering with suction, in a manner similar to that employed in the use of a Gooch. A large part of the tube was allowed to extend into the filtering jar and the connection is made air-tight by means of a short piece of Gooch tubing or a rubber stopper (fig. 1.) It was also found desirable to coat the upper portion of the tube with paraffin so as to prevent the passage of the solution except in the lower half of the filter tube, otherwise the solution will pass down the side of the bell jar.

1. Loc. cit.

FIG 1.

Apparatus used in modified Clay Filter Method.



A 50 cubic centimeters aliquot of humus solution,¹ which represents 1 gram of soil, is drawn through the tube by means of reduced pressure, the filtrate being collected in a short cylinder. After the entire aliquot is drawn through, a 4 per cent solution of ammonia is then passed through so long as it shows any color. Usually about 200 cubic centimeters is required. In no instance have we found it necessary to use more than 250 cubic centimeters. The filtrate and washings are then evaporated to dryness and the determinations completed as usual.

Some difficulty was experienced in completely removing the clay in certain soils. There was found to be considerable difference in different tubes in this respect. Some filters will remove all clay, while others seem to allow a small amount of the most finely divided clay to pass through. After each filtration the tube should be washed out. A test-tube brush was found to be serviceable in removing the clay from the inner walls of the filter tube.

The time required to complete a filtration was found to be about $3\frac{1}{2}$ hours, and by arranging a number of filtering jars in a series an ordinary Richardson pump will provide suction for at least three filters, and with close-fitting connections it is probably possible to operate one-half dozen filters with one pump. In any event, at least one-half dozen solutions can be filtered in one day by this apparatus. No attention is required further than an occasional moment for pouring in solutions and the entire process can be carried out along with other work without interruption.

For the sake of comparison, the results obtained by the official, Hilgard, Mooers-Hampton, Cameron-Breazeale, Rather, and modified clay filter methods are submitted in the following table:

1. The preliminary extractions with hydrochloric acid were made by digesting 10 grams of soil in 200 cubic centimeters of fifth normal hydrochloric acid at ordinary laboratory temperature for 5 hours, filtering and washing free from acid with distilled water, as outlined by Fraps in his directions for co-operative study of humus determination for the Association of Official Agricultural Chemists, May, 1911.

Comparison of several methods with the modified clay filter method.

HUMUS.

Method.	Soil numbers.										
	69.	74.	97.	98.	99.	100.	101.	102.	103.	104.	108.
	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>	<i>Per</i> <i>Cent.</i>
Official.....	4.30	5.94	5.12	6.38	4.64	4.34	6.31	3.54
Hilgard.....	15.63	5.26	2.43	2.61	3.68	2.95	2.71
Mooers-Hampton.....	18.74	5.32	2.68	2.70	3.17	2.32	3.72	3.20	3.72	2.68	3.84
Cameron-Breazeale.	12.30	3.98	2.34	2.38	2.91	2.24	2.85	2.24	2.94	2.36	2.29
Rather.....	20.75	6.49	4.32	4.15	5.01	6.03	5.64	4.38	5.95	4.81	8.24
Modified Clay filter	18.27	5.75	2.64	2.81	3.84	3.48	3.61	3.37	4.74	3.22	3.31

HUMUS ASH.

Official.....	13.25	20.92	10.54	33.20	15.18	13.15	25.42	7.67
Hilgard	5.44	1.85	2.46	2.56	2.00	4.28	1.82
Mooers-Hampton.....	6.33	1.33	.60	.84	.65	.41	1.52	1.70	.98	1.17	0.44
Cameron-Breazeale.	1.09	1.81	.28	.74	.33	.33	.31	.30	.57	.23	.46
Rather	7.71	2.51	12.94	11.43	10.40	25.69	17.61	10.28	20.49	12.74	32.69
Modified Clay filter	2.14	2.19	.54	.75	.57	.64	.78	.70	1.12	.76	.99

From these data it is obvious that the modified clay filter method gives results higher than those obtained in any other method, except the official and Rather methods, neither of which can be relied on with Hawaiian soils. In the Hilgard method a cloudy extract continued to run through the filter paper in some instances so that it was impossible to determine by the color when the extraction was complete. Incomplete extractions, therefore, probably account for the low results obtained by this method. By the use of the method of Mooers-Hampton it was found to be extremely difficult to redissolve all the humus without at the same time deflocculating the clay. In some instances a partial oxidation of humus may have taken place. The Cameron-Breazeale method was also found to be unreliable. By

any of the previously used methods it was extremely difficult to obtain concordant results with the same soil, while with the modified clay filter method concordant results from separate solutions can easily be obtained, and if the method is used with care, it will give reliable results. The following table shows the agreement in duplicate determinations as obtained by this method, using different solutions in each instance:

Duplicate determinations by modified clay filter method.

HUMUS.

Method.	Soil numbers.										
	69.	74.	97.	98.	99.	100.	101.	102.	103.	104.	108.
	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>
Modified Clay filter method.....	18.23	5.76	2.61	2.77	3.87	3.41	3.58	3.33	4.82	3.21	3.30
Do	18.31	5.73	2.60	2.85	3.81	3.55	3.64	3.41	4.67	3.23	3.31

HUMUS ASH.

Modified Clay filter method.....	2.38	2.22	0.57	.53	0.60	0.55	0.84	0.73	1.10	0.79	0.96
Do	1.89	2.15	.50	.97	.57	.74	.72	.68	1.13	.74	1.03

In co-operation with the Association of Official Agricultural Chemists it was found that the clay in some Texan soils can be readily coagulated by the use of ammonium carbonate. In one instance the clay in a humus solution, which gave an ash of 34.59 per cent by the official method, was completely coagulated by the use of 0.5 gram of ammonium carbonate per 100 cubic centimeters, so that the humus ash in the resulting solution was 0.14 per cent. The use of similar amounts of ammonium carbonate in the humus solutions from some Hawaiian soils effected no coagulation of clay whatever. In certain of the soils, however, it was found possible to partially remove the clay with this amount of ammonium carbonate and this behavior suggested the use of still larger quantities of ammonium carbonate. After a number of trials, it was found that ammonium car-

bonate at the rate of 4 grams per 100 cubic centimeters, upon standing, effected a complete coagulation of the clay in all the soils examined, except Nos. 69 and 99. The results obtained by the use of the modified clay filter method, Rather method, and Rather modified method, using 4 grams ammonium carbonate to 100 cubic centimeters, are submitted in the following table:

*Comparison of Different amounts of ammonium carbonate
with modified clay filter method.*

HUMUS.

Method	Soil numbers.										
	69.	74.	97.	98.	99.	100.	101.	102.	103.	104.	108.
	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>
Rather.....	20.75	6.49	4.32	4.15	5.01	6.03	5.64	4.38	5.95	4.81	8.24
Rather modified.....	19.34	4.90	2.42	2.41	3.44	3.16	3.37	3.25	3.77	3.20	3.11
Modified clay filter	18.27	5.75	2.64	2.81	3.84	3.48	3.61	3.37	4.74	3.22	3.31

HUMUS ASH.

Rather.....	7.71	2.51	12.94	11.43	10.40	25.69	17.61	10.28	20.49	12.74	32.69
Rather modified.....	6.26	1.84	.19	.18	2.11	.13	.81	.10	.24	.18	.13
Modified clay filter	2.14	2.19	.54	.75	.57	.64	.78	.70	1.12	.76	.99

From these data it is evident that by the use of sufficiently large amounts of ammonium carbonate a complete coagulation of clay was brought about in most instances, but by comparing the percentages of humus obtained with those from the use of the modified clay filter method, it appears that a partial precipitation of the humus also took place, and in all the samples examined the use of sufficient ammonium carbonate to bring about complete coagulation of the clay, has resulted in the partial precipitation of organic matter also. In some instances the coagulated clay, after washing with a dilute solution of ammonia containing ammonium carbonate, until no residue was left upon evaporating a small portion of the filtrate to dryness,

still contained organic matter soluble in 4 per cent ammonia, thus showing that some humus may be precipitated along with the clay by ammonium carbonate.

In this connection, the question arises as to why it is that ammonium carbonate will completely coagulate the clay in some soil solutions, while in others little or no coagulation takes place. The use of 0.5 gram of ammonium carbonate per 100 cubic centimeters has been found to completely coagulate the clay in Texas¹ soils, whereas in Hawaiian soils little or no coagulation takes place. With the use of considerably larger quantities of ammonium carbonate, however, a complete coagulation takes place in some soils, while in others only partial coagulation can be thus brought about. Alkalis, as is well known, cause a deflocculation of finely divided particles in solution, while acids and certain salts bring about coagulation. It has been found that various calcium salts affect suspension of these soils in water in varying degrees. In some soils a complete coagulation can be produced by a solution of calcium hydrate, carbonate, or sulphate, while in others the carbonate and hydrate have little effect. In solutions containing ammonia such coagulation by lime compounds is uniformly slower.

The behavior of these solutions suggests a fundamental difference in the composition of the clay. As mentioned above, in certain instances ammonium carbonate, at the rate of 4 grams per 100 cubic centimeters, brought about the coagulation of a large part of the clay, but a turbid solution still remained. In such instances the coagulated clay was filtered out and dried and the remaining turbid solution then evaporated to dryness. The residues thus obtained were analyzed with the following results:

Composition of clay from humus solutions.

COAGULATED BY AMMONIUM CARBONATE.

Constituents.	Soil numbers.			
	99.	101.	106.	108.
	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>	<i>Per Cent.</i>
Silica (SiO_2).....	29.00	22.24	25.33	23.80
Ferric oxid (Fe_2O_3)	33.12	37.33	30.42	31.16
Alumina (Al_2O_3)....	37.38	34.93	34.91	37.84

UNCOAGULATED BY AMMONIUM CARBONATE.

Silica (SiO_2)..	38.21	38.29	46.01	1
Ferric oxid (Fe_2O_3)	37.39	43.17	32.57	1
Alumina (Al_2O_3)..	23.40	18.14	21.42	1

1. All the clay in sample 108 was coagulated by ammonium carbonate.

The composition of the coagulated and the uncoagulated clay is thus shown to be considerably different. In every instance the clay was found to contain relatively high percentages of iron, and that part which was coagulated appears to be made up of a mixture of ferric hydrate and silicate of aluminum, both of which doubtless occur in the humus solution in the hydrated state. The uncoagulated suspension contains relatively more silica and iron, and correspondingly less aluminum. The fact that the iron and alumina were found to be present in about the proportions necessary for the formation of a double silicate, together with the behavior of this suspension, suggests the occurrence of such a compound in these solutions. At any rate, the composition of the clay as expressed above suggests a reason for the failure of the Rather method for the determination of humus in these soils.

GENERAL DISCUSSION.

The results of this investigation show that the percentages of humus found in a given soil may vary greatly, depending

largely upon the methods used and the type of soil under investigation. The chief difficulty to be overcome is the separation of humus from clay, and with Hawaiian soils the only method found by which the separation could be made, involved the use of a clay filter. A modification in the concentration of the organic constituents will take place upon passing the humus solution through a clay filter, but this can be overcome by first making the solution to volume then drawing a definite aliquot through the filter, followed by (drawing through the filter) a dilute solution of ammonia until the filtrate contains no organic matter. With the use of a clay filter, modified as previously outlined, concordant results can be obtained, and by a little experience, the details of manipulation can be so perfected as to require a minimum of attention. It is believed that this method can be applied to any soil, and being both practical and accurate, and at the same time involving the use of ordinary laboratory equipment, it can be found useful in any ordinary soil laboratory.

The difficulties attending the use of a number of the older methods are due to the nature of the clay itself. Clay is a very general term, and is usually separated from the other particles by methods which take advantage of the fact that it will remain in suspension for some time, but the exact chemical and physical properties of clay are very variable. The term clay, as used in mechanical soil analysis has reference to the fineness of division, and when unqualified, has reference to no other property. In Hawaiian soils the clay is composed of a mixture of substances which mixture varies between wide extremes. In some instances there is evidence of the existence of a double silicate of iron and aluminum which compound is extremely finely divided and resists coagulation to a remarkable degree. The clay of practically all Hawaiian soils contains a large percentage of iron, a part of which exists as ferric hydrate. This ferruginous character makes the clay extremely difficult to remove from the solution, but enables the analyst to determine whether all the clay is separated from the humus by means of the red color imparted to the humus ash. When the separation has been complete, the humus ash is usually gray. In humus determinations it is of great importance also to know the mechanical structure of the soil, for the applicability of the various

methods depends very largely on the type of soil. Attention is also called to the necessity for reporting the humus ash. From the recent investigation of Wells and others,¹ the use of a centrifuge gives promise of wide application in humus determinations, but unfortunately, these authors did not report either the mechanical composition or the humus ash in the soils examined. So long as humus determinations are made without showing the percentages of humus ash, just so long will uncertainty be felt regarding the accuracy of the results.

A BRIEF STUDY OF THE HUMUS SOLUTION.

The humus solution contains a complex mixture of substances, and although the general usage apparently does not always take cognizance of this fact, it is well known to be true. In connection with the investigation of methods for the determination of humus, certain observations have been made and a brief study of some of the properties of humus solutions from Hawaiian soils has been undertaken and are briefly reported here.

COLOR OF HUMUS.

The color of humus extract is usually a shade of dark brown or black and frequently the color of the humus solution is used as a qualitative test by which the relative amounts of humus in soils are estimated. The percentages of humus are generally greater in the soil than in the subsoil. In a set of two samples of soil and subsoil from the Haiku district of Maui, the soil was of the dark color and resembled what is usually called clay loam, while the subsoil answers to the description of yellowish clay. The general appearance of these samples indicates far more humus in the soil than in the subsoil. Upon extraction with a 4 per cent solution of ammonia, the resulting solution from the soils, when freed from clay, were dark brown, while the humus solutions from subsoils were of a yellowish straw color. The amounts of humus would ordinarily be confidently expected to be greater in the solution from soils, but the actual determinations showed the reverse condition. The following table represents the percentage of humus as found in these solutions:

1. Rather, loc. cit.

Humus in soils and subsoils.

Serial Number.		Humus.	Humus Ash.
		<i>Per Cent.</i>	<i>Per Cent.</i>
105	Soil	2.36	0.44
109	Subsoil	2.75	.73
107	Soil	2.50	.32
110	Subsoil	3.03	.73

These soils were taken from fields that had been cultivated in sugar cane some 20 years ago, but which were afterwards used for grazing purposes, until about 6 years ago, when the land was planted in pineapples. Geologically these soils are of recent formation, although the formation is perhaps as old as that of any other part of Maui. The climate is semihumid, the annual rainfall being about 60 inches. It has been many years since the tropical vegetation was displaced by the cultivated species. The pasture lands there are now occupied largely by grasses, principally Hilo grass.

It was found that the solutions from the soil, when diluted three times, gave about the same intensity of color as those from the subsoil without dilution, although the solution from the subsoil actually contained more organic matter than did those from the soil.

PRECIPITATION WITH HYDROCHLORIC ACID.

A method some times used in the determination of humus consists in precipitating the solution with hydrochloric acid. The precipitate thus obtained is often referred to as "humic acid," and by this method so-called pure humus is sometimes obtained. Upon acidifying humus solutions from these soils with hydrochloric acid, a precipitate was obtained which was separated from the solution by filtration, then redissolved in ammonia, evaporated to dryness, and incinerated. The results thus obtained were as follows:

Organic matter precipitated by hydrochloric acid.

Solutions.	Organic matter.	Ash.	Solution.	Organic matter.	Ash.
	<i>Per Cent</i>	<i>Per Cent.</i>		<i>Per cent.</i>	<i>Per Cent.</i>
Soil.....	0.46	0.08	Subsoil.....	0.14	0.12
Subsoil.....	.21	.25	Soil.....	.54	.09
Soil.....	.25	.05	Subsoil.....	.17	.20

The amounts of organic matter precipitated from these solutions is here shown to be only a small part of the total organic matter in the same. An interesting point in this connection is the fact that while the humus was found to be greater in the subsoil than in the soil, the percentages of organic matter precipitated by hydrochloric acid were greater in the solutions from the soils. In no instance was there more than 25 per cent of the total organic matter present in these solutions precipitated by hydrochloric acid. The fact that relatively more organic matter was precipitated from the soil solution than from the subsoil solution indicates a fundamental difference in the composition of the solutions themselves.

OTHER PROPERTIES OF HUMUS SOLUTIONS.

It has been observed in the course of our experiments, that not all humus solutions are affected to an equal degree in passing through a clay filter. The ammonia solutions from some soils have been found to undergo little or no change, in so far as the total amount of organic matter which they contain is concerned, while still others become greatly modified. In some instances a change in concentration, equal to almost 50 per cent of the total organic matter present, takes place, and in such instances an increasingly large amount of ammonia is required in the modified clay filter method, in order to insure a complete removal of the organic matter; in other words, some compounds occurring in humus solutions are absorbed and perhaps dialyzed to a much greater extent than are others. This property is in harmony with the common knowledge of organic compounds.

In attempting to coagulate the clay by means of large amounts of ammonium carbonate, it was further observed that in certain instances a flocculant precipitate, afterwards found to be organic, was formed, while in other solutions, which contained equally as much total organic matter, no precipitate was formed. In this connection, it is of interest to note that the precipitates obtained by the addition of certain salts to humus solutions from different soils have been found by Fraps and Hamner¹ not to be proportional to the organic matter in the humus solutions and to vary in some degree when salts of different bases are used.

In the preliminary treatment with hydrochloric acid, the extracts from several soils used in these experiments appeared to contain organic matter, and upon precipitating these with ammonia, by means of which the iron is removed, these solutions were found to contain organic matter, in one instance, in considerable quantities.

The humus from various soils has been found to vary greatly in elementary composition. Hilgard² points out that the percentages of nitrogen in humus in arid climates is considerably higher than that from humid sections. The writers have found some variations in the percentages of nitrogen in humus from Hawaiian soils when taken from sections where very similar climates prevail. The carbon content is anything but constant. From the results of a number of investigations, the carbon content of humus has been found to vary from 35 to 65 per cent of the humus. With such variation a corresponding variation is found in the hydrogen and oxygen. Similarly, the mineral matter chemically combined with humus also varies considerably. By reference to a previous table (p. 12) it will be seen that the mineral matter in soil No. 74 is relatively much greater than that of soil No. 69, that of the former being found to be 38.5 per cent of humus, while the latter contained 13 per cent. Soil No. 74 was taken from the Parker ranch on the slopes of Mauna Kea, at an elevation of about 4,000 feet, and while this soil doubtless originated under a humid climate, the amounts of rainfall in this section have been very small during historic times. The soil has perhaps been in the process of formation

1. Loc. cit.

2. Loc. cit.

for centuries. Soil No. 69, on the contrary, came from the Nahiku district of Maui, from land recently cleared of a dense tropical jungle, where the rainfall approximates 200 inches per annum. The organic matter in this soil may be looked upon as being in a much less advanced state of decomposition than that of soil No. 74.

From the foregoing brief observations, it is apparent that the fundamental nature of humus is extremely variable. Without doubt humus extracts from soil solution contain a complex mixture, susceptible of alteration in varying degrees by the use of simple means, but whose exact composition is far from being understood.¹ The studies reported have been preliminary to a more fundamental investigation of the several chemical bodies which comprise the humus solution.

THE USAGE OF THE TERM HUMUS.

In agricultural writings the usage of the term humus is far from being uniform.² The term humus came into use as a result of the announcement of Berzelius in 1838, who claimed to have isolated a definite chemical body from soils called by him, humin, which body he claimed to have definite properties. As has been pointed out by Schreiner and Shorey,³ this work was done before the days of modern organic chemistry, and subsequent investigations have failed to establish the presence of such a definite chemical substance. The terms humic acid and humates have come into use from the fact that certain properties of so-called humus were interpreted as indicating the existence of definite derivatives of this hypothetical substance. Recent investigations and the general properties of so-called humus, together with its extreme variability, show that there are, in reality, no such substances in the sense in which they are used.

The definitions of the term humus, as given by various authorities, are far from being the same. Some authorities make

1. Soils. New York and London, 1907, p. 135.

2. With the exception of the recent work of Jodidi (Michigan Sta. Tech. Bul. 4 and Iowa Sta. Research Bul. 1) and that of the Bureau of Soils of the U. S. Department of Agriculture (Buls. 47, 53 and 74), very little can be said to be known concerning the chemistry of soil organic matter. It is of interest in this connection that the isolation of the first definite chemical organic body from soils was made by Shorey from a Hawaiian soil (Hawaii Sta. Rpt. 1906, pp. 37-59), which in many respects is similar to soil No. 69.

3. U. S. Dept. Agr., Bur. Soils Bul. 53.

the term synonymous with vegetable mold; others refer to it as partially decayed organic matter. Hopkins¹ in a recent address is quoted as saying that humus is the part of soil organic matter that is resistant to decay and that humus in and of itself furnishes nothing to feed plants. In another publication² he states that humus means decaying organic matter which contains the nitrogen of importance in soils.

The definition frequently given of humus is that it is the soil organic matter soluble in dilute ammonia after removing the calcium and magnesium. The indiscriminate use of the term humic acid and humates has no foundation in scientific fact, and while this fact is usually recognized, the usage is such as to imply the existence of definite chemical substances.

In reality, humus is a no more definite expression than is mineral matter, and the use of the designations humic acid and humates has no justification. The fact that mineral bases, like calcium and magnesium, combine with certain soil organic constituents of humus to form precipitates, does not imply that the resulting substances thus formed have simple salt-like properties, nor that the substances with which the base is combined are of an acid nature in a truly chemical sense.

The chemical nature of soil organic matter has been recently extensively studied by Schreiner and Shorey and Jodidi, and sufficient data have already been obtained to show the extreme complexity of the mixture. Until we have more definite knowledge concerning the substances comprising the organic matter of a soil, the specific effect produced by it and the functions performed in the soils will necessarily be guess-work.

1. Breeders' Gaz. 59 (1911), p. 558.

2. Illinois Sta. Cir. 116, p. 5.

